Argonne Hational Laboratory

THE SEPARATION OF MICROGRAM QUANTITIES

OF 252
98 Cf AND 248
96

BY EXTRACTION CHROMATOGRAPHY
IN A HIGH-LEVEL CAVE

by
E. P. Horwitz, C. A. A. Bloomquist,
J. A. Buzzell, and H. W. Harvey

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Gincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
Iowa State University
The University of Iowa

Kansas State University
The University of Kansas
Loyola University
Marquette University
Michigan State University
The University of Michigan
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame

The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
University of Texas
Washington University
Wayne State University
The University of Wisconsin

- LEGAL NOTICE -

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois 60439

THE SEPARATION OF MICROGRAM QUANTITIES OF 252 Cf AND 266 Cm BY EXTRACTION CHROMATOGRAPHY IN A HIGH-LEVEL CAVE

by

E. P. Horwitz, C. A. A. Bloomquist, J. A. Buzzell, and H. W. Harvey

Chemistry Division

February 1969

TABLE OF CONTENTS

		Page
ABS	STRACT	4
I.	INTRODUCTION	4
II.	EXTRACTION CHROMATOGRAPHY OF Cm(III) AND Cf(III) WITH HDEHP	5
III.	EQUIPMENT	7
IV.	PROCEDURE	9
	A. Preparation of Column Material and Columns B. Chromatographic Separation	9
v.	Cities the street has at 10 as at 10 Con from Stot Debug FIDERP	11
API	PENDIX	13
ACI	KNOWLEDGMENT	15
REI	FERENCES	16

LIST OF FIGURES

No.	Title	Page
1.	Concentration of Hydrogen Ion for the Elution of Cm(III) and Cf(III) from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed; Flowrate ~ 1.2 ml/cm ² /min, 60°C	6
2.	The Elution of Cm(III) and Cf(III) with 0.41 \underline{N} HCl from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1.3 ml/cm²/min, 60°C. Column bed size: 0.0620 cm² x 10 cm; bed density: 0.371 g/ml; drop volume: 39 μ 1/drop; f = 0.72	6
3.	Inside View of Containment Box	7
4.	Back of Containment Box Showing Transfer Port and Can-out System	8
5.	The Separation of 10 μg of $^{246,248} Cm$ from $^{252} Cf$ Using HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1 ml/cm²/min; 60°C. Column bed size: 0.0638 cm² x 10 cm; bed density: 0.412 g/ml; drop volume: 41.7 $\mu l/drop; f$ = 0.72 .	11
	TABLE	
No.	Title	Page
I.	Separation Factor, Cf(III)/Cm(III), for the Extraction Chromatography System HDEHP on Celite	5

THE SEPARATION OF MICROGRAM QUANTITIES OF 252 Cf AND 248 Cm BY EXTRACTION CHROMATOGRAPHY IN A HIGH-LEVEL CAVE

by

E. P. Horwitz, C. A. A. Bloomquist, J. A. Buzzell, and H. W. Harvey

ABSTRACT

The extraction chromatography technique was applied to the separation of microgram quantities of ²⁴⁸Cm from hundred-microgram quantities of ²⁵²Cf. Di(2-ethylhexyl) orthophosphoric acid adsorbed on hydrophobic Celite was used as the column material. Dilute nitric and hydrochloric acids were used as the elutriants. Column runs were performed in a high-level cave with 48-in. concrete shielding. Decontamination factors of ²⁵²Cf from the ²⁴⁸Cm of 10⁸-10⁹ were obtained in a single-column run.

I. INTRODUCTION

During the last few years microgram to milligram quantities of the isotope $^{252}_{98}\mathrm{Cf}$ (alpha half-life of 2.65 yr) have become available from the Oak Ridge National Laboratory. The primary uses of this isotope have been as a neutron source, as a result of its 85-yr spontaneous-fission half-life, and as a target for the production of einsteinium by neutron irradiation. However, as larger quantities of $^{252}_{98}\mathrm{Cf}$ become available, another important use of this isotope will be as a source of $^{248}_{96}\mathrm{Cm}$, which is the daughter of $^{252}_{98}\mathrm{Cf}$ and is one of the most stable isotopes of curium. Its alpha half-life (3.84 x 10^5 yr) and alpha specific activity (8.34 x 10^3 d/min/µg)(Ref. 1) are $>10^4$ times the alpha half-life and $<10^4$ times the specific activity of the most readily available isotope of curium, namely, $^{248}_{96}\mathrm{Cm}$. Because of its stability, $^{248}_{96}\mathrm{Cm}$ is one of the best sources of curium for the preparation and study of the chemical compounds of this element.

This report describes an extremely rapid and efficient method for separating $^{248}_{96}\mathrm{Cm}$ from microgram quantities of its parent, $^{52}_{98}\mathrm{Cf}$. The separation is based on the large difference in the extractability of Cm(III) and Cf(III) by the extractant di(2-ethylhexyl) orthophosphoric acid (HDEHP). The $^{248}_{96}\mathrm{Cm}$ and $^{252}_{98}\mathrm{Cf}$ are separated on an extraction chromatography column containing HDEHP. Because of the large number of neutrons emitted by

THE SEPARATION OF MICROGRAM QUANTITIES OF THE AND THEM BY EXTRACTION CHROMATOGRAPHY IN A HIGH-LEVEL CAVE

E. P. Horwitz, C. A. A. Bloomsgalat, J. A. Bussell, and H. W. Harvey

ABSTRACT

The extraction chromatography technique was spalled to the separation of inderegram quantities of ****Con free bundred-microgram quantities of ****Con free orthophosphoric acid adsorbed on hydrophobia Cellic was used as the column material. Dilute nitric and hydrochloric acids were used as the clutriants. Column runs were performed in a high-level cave with 48-in, concrete shielding. Decontamination factors of ***Column the ***Column runs were obtained in a single-column run.

LINGE DESCRIPTION

During the last lew years microgram to milligram quantities of the factors \$\frac{2}{2} \tilde{C} \tilde{C

This report describes an extremely rapid and efficient method for separating of the from interogram quantities of its pareint, SeCh. The separation is based on the large difference in the extractability of Cm(III) and Cf(III) by the extractant difference in the extractability of Cm(III). The selfum and office are expanded on an extraction chromatography column containing HDEHP. Because of the large number of neutrons smarted by

microgram quantities of $^{252}_{96}$ Cf, it is necessary to perform the separation by remote control in a high-level cave. A containment box within the cave houses the equipment and apparatus used for the separation.

II. EXTRACTION CHROMATOGRAPHY OF Cm(III) AND Cf(III) WITH HDEHP

The conditions for "milking" microgram quantities of \$^{252}_{98}Cf for its daughter \$^{248}_{96}Cm are based on extensive tracer-scale data on the extraction chromatography of Am(III), Cm(III), Bk(III), Cf(III), Es(III), and Fm(III) with HDEHP, which has been obtained by the authors \$^{2,3}\$ during the last few years. The column material consisted of HDEHP adsorbed on a hydrophobic diatomaceous earth support (Celite-545) (see Sect. IV). Many column parameters were evaluated in these studies; however, only the data that are pertinent to the Cm-Cf separation will be presented here. The tracer-scale Cm-Cf data, together with some data for americium and berkelium, will be published in a more complete form elsewhere.

Table I shows the separation factor Cf(III)/Cm(III) at four different temperatures obtained with dilute HNO_3 and HCl elutriants. The column contained 88.2 mg HDEHP/g of dry bed. The separation factors were calculated by use of the equation

$$C = (V_{\text{max}} - v_{\text{m}})/v_{\text{m}}, \tag{1}$$

where V_{\max} is the volume of eluate to peak maximum, v_{\min} is the void volume or volume of the mobile phase, and C_{\min} is the number of free column volumes to peak maximum.

TABLE I. Separation Factor, Cf(III)/Cm(III), for the Extraction Chromatography System HDEHP on Celite

Temp, °C	HNO ₃ Elutriant	HCl Elutriant		
25	26	32		
45	24	28		
60	22	25		
75	20	23		

The data in Table I show that the separation factor is relatively insensitive to temperature. In addition, the difference for HNO $_3$ and HCl is also very small. Since column performance (measured by calculating the plate height) was found to be substantially higher at higher temperatures for Es(III), ² a temperature of 60°C was selected as a convenient temperature at which to carry out the separation of curium and californium.

microgram quantities of "Cf. it is necessary to perform the asparation by remote control in a high-level cave. A containment box within the cave houses the equipment and apparatus used for the reparature.

IL EXTRACTION CHROMA FOCKAPHY OF Control AND GRAIN WITH HIPENEY

The conditions for 'mulking' marriagness or 'CC for its daughter 'CC are been described and the extraction of the constant of

Table 2 shows the separation factor CHIII)/CmBH) or four different temperatures obtained with drive HWO; and HCI clubtrants. The columns contained 88.2 mg HDEHP/g of dry had. The separation factors were called culated by use of the equation.

C = (Vmax - vm)/vm

where V_{max} is the volume of sluste to peak maximum, v_m is the velution volume or volume of the mobile phase, and C is the minder of free volume volume to peak maximum.

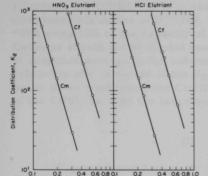
TABLE 1. Separation Factor CI(III) Cm(III) for the Extraction Chromotography System ungree on Colons

The data in Table I show that the separation failer is relatively meanifive to temperature. In addition, the difference for thio, and HCl is also very small. Since column performance (measured by calculating the plate height) was found to be substantially higher at higher temperatures for Ex(III). A temperature of 50°C was selected as a convenient temperature at which to carry out the separation of curtum and calculations.

Figure 1 shows the acid dependency of the Kd of Cm(III) and Cf(III) at 60°C. The column again contained 88.2 mg of HDEHP/g of dry bed. The

values of Kd were calculated by use of

the equations



121-4676

Fig. 1. Concentration of Hydrogen Ion for the Elution of Cm(III) and Cf(III) from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed; flowrate ≃ 1.2 ml/cm²/min, 60°C

Molarity of HNOs

$$V_{\text{max}} = v_{\text{m}} + K_{\text{d}}v_{\text{s}} \tag{2}$$

and

$$K_d = C(v_m/v_s), \tag{3}$$

where Kd is the distribution coefficient and vs is the volume of stationary phase (HDEHP). The value of vs is obtained by dividing the weight in grams of HDEHP in a column by the density of HDEHP (0.975 g/ml). By means of Eqs. 2 or 3 and the data in Fig. 1, the acidity of the elutriant required to elute curium and californium over a wide range of values of Vmax or C can be calculated.

Figure 2 shows a typical Cm(III)-Cf(III) tracer-scale separation. The

values of vs and vm for this particular column were 0.021 and 0.46 ml, respectively. An acid concentration (HCl in this case) was calculated to elute curium in the first free-column volume (C in the range from 0 to 1).

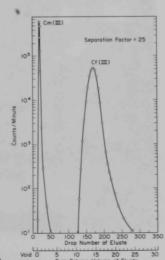


Fig. 2

The Elution of Cm(III) and Cf(III) with 0.41 N HCl from HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1.3 ml/cm²/min, 60°C. Column bed size: 0.0620 cm² x 10 cm; bed density: 0.371 g/ml; drop volume: 39 $\mu 1/\text{drop}$; f = 0.72.

121-4678

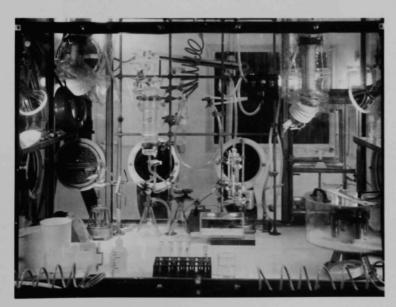




In applying the extraction chromatography system to the separation of μg to mg samples of $^{252}_{96} \text{Cf}^{-248}_{96} \text{Cm}$, the effect of mass on the Kd must also be taken into account. The mass effect was studied using Eu(III) as a substitute for Cf(III). If it is assumed that one mole of Eu(III) [or Cf(III)] complexes six moles of HDEHP, the reduction in the Kd of Eu(III) was ~37% when 12% of the capacity of the column was complexed by Eu(III). Columns should not be loaded much beyond 12% of their capacity because of radiation damage to the column. The Cm-Cf separation should still be relatively efficient even if the Kd of Cf(III) was reduced by 37%. Actually, under these conditions, the Cm(III) band would be readily displaced in front of the Cf(III) band by the large quantity of californium.

III. EQUIPMENT

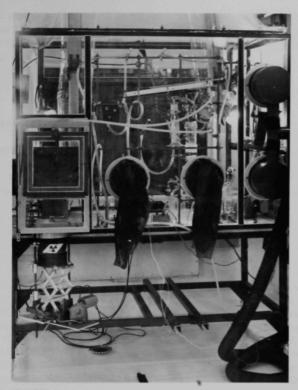
Figures 3 and 4 show the general layout and apparatus employed for performing the Cm-Cf separation by remote control in a high-level cave with 48-in. concrete shielding. The equipment utilized and the materials of construction employed are listed in the Appendix. In most cases standard-size glassware and equipment were used in the containment box. However, in certain situations equipment was modified in order to permit easy handling with the master-slave manipulators.



121-4074

Fig. 3. Inside View of Containment Box



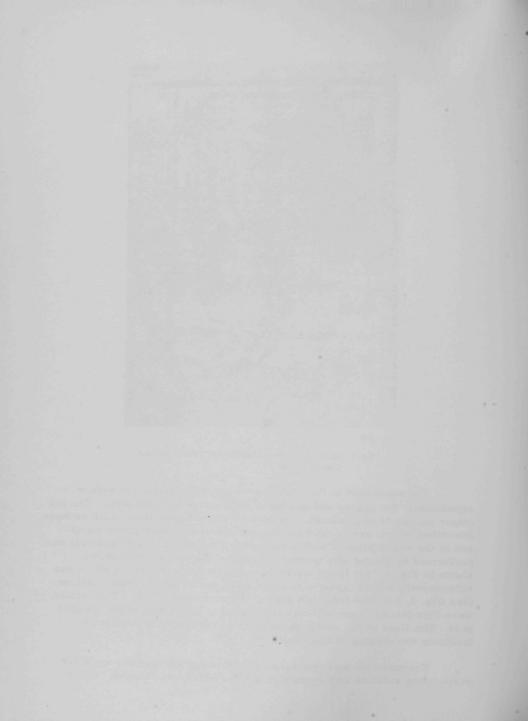


121-4075

Fig. 4. Back of Containment Box Showing Transfer Port and Can-out System

The equipment in the containment box was designed to reduce significantly the causes and spread of radioactive contamination. The two major causes of contamination in remote-control operations, such as those described below, are in the handling and removal of radioactive waste and in the evaporation of highly radioactive solutions. Waste removal was performed by means of a remote one-gallon waste-transfer system, shown in Fig. 4. All liquid waste was absorbed in vermiculite which was subsequently placed, along with other solid waste, in ice-cream cartons (see Fig. 3, extreme front left side of the containment box). The cartons were then placed in one-gallon cans housed in the bottom of the transfer port. The floor of the containment box was covered with Formica to facilitate the cleanup of any "spills."

Evaporations were performed by drawing air over the top of the evaporating solution and up through a tube, which was clamped ~1-2 in.



above the top of the solution. The vapors were then passed from the tube through a trap containing dilute HCl (see Fig. 3). The negative pressure in the evaporation system was maintained by means of a light-duty vacuum pump.

IV. PROCEDURE

A. Preparation of Column Material and Columns

The HDEHP used in preparing the column material was purified following the procedure of Peppard et al. A commercial diatomaceous earth, Celite 545, was used as the solid support for the HDEHP. The Celite was graded by means of a grading apparatus almost identical to that described by Aly and Latimer. The optimum particle-size fraction, which was found by previous studies to have a settling rate of 1.0-1.3 cm/min, was selected for the preparation of the column material. The graded Celite was then made hydrophobic by exposing to the vapors of dimethyldichlorosilane (DMCS) in a vacuum system.

The HDEHP-Celite column material was prepared by mixing the appropriate amounts of graded hydrophobic Celite and purified HDEHP with acetone and evaporating the excess solvent at room temperature. Two column materials of different capacity were prepared. The quantities used in preparing the small-capacity material, which contained 88.2 mg (0.27 mmol) of HDEHP/g of dry column material, were the following: 193 mg of HDEHP, 20-25 ml of acetone, and 2 g of Celite. The large-capacity material, which contained 162 mg (0.50 mmol) of HDEHP/g of dry column material, was prepared as described above except that the quantity of HDEHP was doubled.

Pyrex glass columns (of ~2.8 and 4.0 mm ID) were used for all separations. The columns were exposed a minimum of 30 min to DMCS vapors in a desiccator, then washed with acetone, air dried, and weighed. The bed volume and cross-sectional area of the columns were measured by weighing the volume of water (while in the column) between two marks 10 cm apart. After drying, the columns were filled by gently tamping the dried HDEHP-Celite material to form a bed 10 cm in length. The columns were again weighed to obtain the weight of column material. The volume of the stationary phase, v_s, was then calculated from the quantity of HDEHP on the column (in grams) and the density of HDEHP (0.975 g/ml).

All the columns used for Cm-Cf separations were thermostated at 60°C. The columns were routinely preconditioned with 10 bed volumes of preboiled 0.1 \underline{N} HNO3 or HCl at 18-20°C and at a rapid flowrate. After preconditioning, the columns were thermostated at the proper temperature. All air pockets in the bed were removed by this procedure. The void volume $v_{\rm m}$ was measured by determining the breakthrough of $^{134}{\rm Cs.}$

above the top of the solidies. The vapors were then passed from the tube through a trap containing differ life; if The negative pressure in the evaporation system was maintained by means of a light-duty darroup pumps.

TROCEDURE

The HDER P werd in Preparing the column material was positived following the procedure of Poppardigt al. A commercial distormanceous following the procedure of Poppardigt as the solute support for the HDERP 1960. Celline was graded by means of a gradual explanation and almost about a solution was slowed by means to be attained. The optimum particle-are of a celling that of the column material. The celling of the column material. The celling of the column material.

est selected for the proparation of the column material. The ganded Celiferes then made hydrophobic by exposing to the vapore of dimethyld/chlorositions. DMCS) in a vocuum system.

The MDEHP Cellie column material was propored by mixing the appropriate amounts of graded by traplober Cellie and puriod MDEHP with a column materials of duferent capacity were preparing. The journal capacity meterials which contained 80 city. In proparing the small capacity meterials which contained 80 city.

[0.27 mmol but MDEHP (rot dry column material, were fireful wings of HDEHP. 20 city of actions material, were fireful at argentials and a gold Cellies 10s largently materials, which contained to me (0.00 mmol) of HDEHP, as increased as described above except fint the quantity of HDEHP was doubled.

Pyrex gibes columns were exposed a minimum of 50 min to DMGS vapors in a desircator, then washed with routine, air default and vapors in a desircator, then washed with routine, air default and veryhed vapors in a default and veryhed by weighing the volume and gross sectional area of the columns that was incasting the volume of water (while a line column) between two matters in a pair. After devalue, the columns area littled by gently tamping the dried HDEHE-Collie measured to do do not be very to do column material. The valume of the stationary phase, w. was then exicated from the quantity of the HDEHE on the column in grants and the dealth of the HDEHE (C.97) given)

All the columns used for Could separations were thermostated at 60°C. The columns were continues of preconditioned with 10 bed volumes of probabled 0.1 M MMO, or 1401 at 18120 C and at a rapid Cowrate. After preconditioning, the celturals were their mastated at the proper temperature All air potchets in the bod were removed by that procedure. The vold wolumn of m was measured by determining the breakthough of 1100.

B. Chromatographic Separation

The typical column bed size used for the $^{248}_{96}$ Cm "milking" of 100-250- μ g samples of $^{252}_{98}$ Cf was 0.13 cm² x 10 cm and contained 545 mg of column material (162 mg of HDEHP/g of dry bed). The fractional void volume was 0.70. The values of v_s and v_m were 9.1 x 10^{-2} and 0.91 ml, respectively. By use of Eq. 2 and the data in Fig. 1, the acidity of elutriant required to elute curium in the first 0-2 free column volumes of eluate was calculated to be 0.46 \underline{N} HNO3. The nitric acid elutriant was selected as the elutriant for use with high levels of alpha activity even though the separation factor is slightly smaller than in the HCl system. At this acidity, the value of V_{max} for californium would be ~14 free column volumes of eluate. (The value of Kd was reduced by ~10% due to the mass of the samples.)

The californium sample was evaporated to dryness in a centrifuge tube, dissolved in a minimum volume of 0.3 $\underline{\mathrm{N}}$ HNO₃ (~0.5 ml), and loaded on the column by means of a Berkeley pipet. Several additional 0.5-ml portions of 0.3 $\underline{\mathrm{N}}$ HNO₃ were used to rinse the centrifuge tube and were subsequently loaded on the column. The initial portion of acid used to dissolve the californium sample and the rinses were vortexed thoroughly in the sample tube and finally centrifuged. This procedure improved the efficiency of the loading operation. The efficiency of the loading was easily determined by neutron counting the centrifuge tube which contained the californium sample.

The use of $0.3 \ \underline{N} \ HNO_3$ for loading and rinsing insured rapid diaplacement of the curium band away from the californium band. A few minutes after loading the californium sample on the column, the intense alpha and spontaneous-fission activity of the $^{252}_{98}$ Cf produced noticeable gas pockets in the column. After loading, the elutriant was changed to $0.46 \ \underline{N} \ HNO_3$. The flowrate was ~1-2 ml/cm²/min. Approximately 99.5% of the curium eluted from the column in the first three free column volumes of eluate. The elution was usually continued for six free column volumes before stripping the californium from the column with $1 \ \underline{N} \ HNO_3$. Approximately three free column volumes of $1 \ \underline{N} \ HNO_3$ removed ~99.9% of the californium from the column.

The californium samples were usually evaporated to dryness and loaded on a cation exchange column (Dowex 50W, X-8) with 0.1 \underline{N} HCl. (The cation exchange column was ~4 mm ID by 10 cm in length.) After loading, the column was eluted with 2-3 bed volumes of 2 \underline{N} HCl. The californium was then stripped from the column with ~5 bed volumes of 6-7 \underline{N} HCl. The californium samples were allowed to stand in 6-7 \underline{N} HCl solution until the next $^{248}_{96}\text{Cm}$ separation. The purpose of the cation cleanup column was to remove from the californium any radiolytic decomposition products of the HDEHP which might be present, e.g., H_2MEHP or H_3PO_4 .

Chromatographic Separation

The typical column bed size insed for the 250 m and contained 545 mg. 100-250-198 samples of 250 was 0.13 cm x 10 cm and contained 545 mg. of column material (162 mg of 1951). It can be d. The trachemit value of column material (162 mg of 1951). The values of grand vm were 9.1 x 10 and 0.31 cm volumn was column to be 0.45 m the first 0-2 free column volumns of chartened as column to be 0.45 m 1900-215m mixed acid chartened as colored as the call the first use with high levels of sipha activity even though the call acids the call the value of V max for callers in a find the value of V max for callers and does 14 free column of the value of the value of the was colored by 100 due to the max of the value of the value of the was colored by 100 due to the max of the value.

The californium sample was evaporated to dryness in a centringe unbe, distributed as a minimizer column, distributed as a minimizer column of 0.3 N 1100, (*0.5 ml) and landed on the column by means of a Berkeley plant. Several additional 0.5-ml and portions of 0.3 N HNO, were used to rinse the centrifuge tube and week column. The initial portion of add used to distribute the californium sample and the ringed were vertexed therefore the central column of the distribution of the distribution of the californium constitute of the centrifuge tube which contains the centrifuge tube which contained the californium sample.

The use of 0.3 M livo, for loading and rivalng insured tapid displacement of the curious band away from the californium band. A new columns after loading the californium sample on the column, the californium sample on the columns the column. After loading, the electricat was charged to 0.50 m livo. The flowrate was 1.2 ml/cm/min approximately 98.0% of the curious states from the columns of cludic. The cludical was usually continued for hix received volumns before stripping the californium from the columns with 1 M livos approximately three trace columns of the livos the columns with 1 M livos approximately three trace columns of the livos the columns that the columns that the columns to the columns that the columns the columns that the columns is the californium from the columns.

The californian samples were usually evaporated to diversible loaded one carton exchange column (Dower 50W, N. 8) with 0.1 2 MRC of the cation exchange solumn was re mm iD by 10 cm in dength.) After californian was returned with 2-3 bed volumes of 2 MRC. The californian was clumn with 2-3 bed volumes of 2 MRC. The californian was then stripped from the column with 5 bed volumes of 6-7 M MC. The californian was to the californian samples were allowed to stand in 6-7 M MC. Solumn was to remove from the californium any radiulytic decomposition products of the MDEHR which might be present, e.g., Hamilip or HPO.

The separated ²⁴⁸₉₆Cm fraction was removed from the high-level cave and further purified by extraction chromatography using HDEHP on Celite. The column size and conditions are similar to those shown in Fig. 2.

V. RESULTS AND DISCUSSION

The curium fractions (first three free column volumes) from the first HDEHP column were consistently decontaminated from $^{258}_{98}\mathrm{Cf}$ by a factor of 10^8 - 10^9 . Unfortunately, the $^{252}_{98}\mathrm{Cf}$ samples were also contaminated with other californium isotopes, namely, $^{249,250,251}_{98}\mathrm{Cf}$, which amounted to ~25% of the total californium by mass. Thus, the final curium product contained other curium isotopes. A typical curium fraction contained ~10-12 μg of curium, 96% $^{248}_{96}\mathrm{Cm}$ -4% $^{246}_{96}\mathrm{Cm}$ by mass and 21% $^{248}_{96}\mathrm{Cm}$ -79% $^{246}_{96}\mathrm{Cm}$ by activity.

The procedure described above was also used to separate $^{244}_{96}\mathrm{Cm}$ from the californium samples prior to the "milking" experiments. The decontamination of $^{244}_{96}\mathrm{Cm}$ from $100\text{-}250\text{-}\mu\mathrm{g}$ samples of californium was $\geq 10^3$, depending on the efficiency of loading and rinsing of the reservoir. The $^{246}_{96}\mathrm{Cm}$ content in the $^{246}_{96}\mathrm{Cm}$ was maintained at <1% by activity ($<10^{-4}\%$ by mass). During the purification of the californium samples, care was taken to minimize contamination of equipment in the containment box with $^{24}_{96}\mathrm{Cm}$. Such contamination could result in cross-contamination of $^{246,249}_{96}\mathrm{Cm}$ samples with $^{246}_{96}\mathrm{Cm}$.

Figure 5 shows the final purification of 10 μg of $^{246,248}_{96} \text{Cm}$ from any traces of alkali and alkaline earth metals present and from any remaining $^{252}_{98} \text{Cf}$. The final $^{246,248}_{96} \text{Cm}$ product was spectroscopically pure (>99.9%)

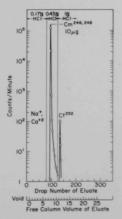


Fig. 5

The Separation of 10 µg of 246 , 248 Cm from 252 Cf Using HDEHP on Celite: 88.2 mg of HDEHP/g of Dry Bed, Flowrate: 1 ml/cm^2 /min; 60° C. Column bed size: $0.0638 \text{ cm}^2 \times 10 \text{ cm}$; bed density: 0.412 g/ml; drop volume: 41.7 µl/drop; f = 0.72.

121-4181

The separated in traction was removed from the high-level ave and further perfice by extraction chromatography using highly on Collection column size and conditions are similar to those shown in Fig. 2.

V. RESTRICTS AND DISCUSSION

The curium tracitions (first three column volumes) from the distribution of the first three free columns volumes are consistently decontained from files by a factor of 10°-10°. Unfortunately, the files samples were also contained to with other californium isotopes, samply, and and four the total californium by mass. Thus, the final custom product contained contained other custom factors. A typical custom fraction contained cities are custom. For the file of the file of

The procedure described above was also used to separate of the from the californium analysis prior to the "milking" experiments. The decomanization of "Com trans 100-250 ug samples all californium was = 10 depending on the efficiency of loading and running of the reservoirs. The depending on the efficiency of loading and running of the reservoirs. The first was maintained at \$\(\text{IV}\), by well-like \$\(\text{CIO}^2\) by well-l

Figure 5 shows the final purification of 10 ug of configuration from any remaining traces of alkali and alkaline earth metals present and from any remaining traces. The final remaining product was spectroscopically pure (299,9%)



The separation of the particle of the state of the state

ratio rei

from all impurities. (High-purity HCl solutions were used in the final elutions.) Thus, the extraction chromatography method with HDEHP not only decontaminated the californium from curium by many orders of magnitude ($>10^{10}$), but also gave a final product that was suitable for the preparation of curium compounds.

Although the largest quantity of $^{252}_{98}$ Cf that was "milked" for $^{248}_{96}$ Cm was 250 μ g, the column size and capacity employed should handle up to 1 mg of $^{252}_{98}$ Cf. Even larger samples of californium (e.g., up to 100 mg) could be "milked" in the above cave facility by increasing the column dimensions.

8 (

from all impairities. (Figh-purity HCI solutions were used in the final solutions.) Thus the extraction chromatography metaod with PDEHP and only decompanied the calliarman from curtain by many orders of conguityde (>10°), but also gave a final product that was further for the proparation of curtam compounds.

Although the largest quantity of "ict that was 'milled' for "illow was abby go, the column error and capacity employed should handle up to 1 mp of "ict. Even larger samples of a therefore (e.g., up to 100 mg) could be "maliced" in the above cave (a.t)th by intreacing the column dimensions.

APPENDIX

Equipment and Materials

1. Containment Box

a. Construction

- (1) Size: 4 ft deep, 6 ft wide, and 4 ft high
- (2) Materials
 - (a) Aluminum floor plate and panels covered with No. 949 white Formica
 - (b) Lucite wall sheeting
 - (c) PVC corner and joining materials
 - (d) Unistrut reinforcing
 - (e) Plywood pallet, painted with fire-resistant paint
 - (f) RTV silicone caulking
 - (g) Urethane gaskets on transfer port and front panel
- (3) Boots for manipulators
 - (a) Upper boot: PVC, 0.012 in. thick
 - (b) Lower boot: PVC, 0.006 in. thick
 - (c) Gaultlet: Hyperlon-coated urethane
- (4) Double-door transfer porch: 12- x 12- x 9-in, transfer door
- (5) Gloves on side and back of box for decontamination

b. Ventilation for Containment Box

- (1) Inlet filters: 8-in. diameter x 6 in. thick; absolute filters (99.95% efficient)
- (2) Exhaust filters: 8-in. diameter x 6 in thick; absolute filters (99.95% efficient)
- (3) Negative pressure as per manometer = 0.250 in. of water

2. Apparatus in Containment Box

- a. Vortex mixer
- b. Self-illuminated magnifying glass
- c. Lucite tube holder for neutron counting
- d. Evaporation apparatus, in-box traps, and in-line scrubber
- e. Berkeley pipet line and glass ball-joint connector
- f. Nitrogen pressure line and glass ball-joint connector for columns
- g. Thermostated column jacket (dc coil heated) and extraction chromatography column
- h. Photoelectric-beam drop-counting device
- i. Sliding fraction collector

350 EN 39 A

Equipment and State or in b

Confining out Box

Constitution

(1) Siste 4.ft deep 6 few

alsitettal

(a) Alumina in floor plate and pariols covered with No. 945 white Foreign

go isgada link dirand (d

c) PVC curner and joining materials

guiotalifier intilizali (b)

(e) Plywdod gallet, painted with fire-resistant paint

(f) RTV silvers canifer

(g) Ure Couls ratikets on transfer port and from panel

(a) Harardon Puc A of Section

(a) Uppersoon, PVC, U,UA inclinish

(b) Lower Poor RVC, 0 006 in direk

(4) Double-door transfer porch; 12- x 12- x 9-in; transfer, door

Gloves on side and back of box for decoutsmination

Ventilation for Containment Box

(1) Injet filters, 3-in, diameter x 6 in thick, absolute filters (99.95% election)

(2) Exhaust filters: 8-m. diameter y n in thick, absolute filters (49, 98% effected)

3) Negative presinge as per manameter = 0 250 m, of waler.

Apparatus in Containment Box

a. Vortex mixer

b. Self-limminated magnitying glass .

Lucuis lube holder for neutron countr

d. Evaporation apparatus, in-box traps, and ta-line scrubber

Borkeley pipet line and glass ball-joint connector

t. Mitrogen pressure line and glass ball-joint connector for columns.

Thermostated column sector (do coil heated) and exitaction

Photoelectric-beam drop-country device

Siding fraction collector

- j. Teflon 3-way stopcock valve nitrogen pressure line selector
- k. Distilled water line containment box inlet
- 1. Plexiglas-shielded centrifuge
- m. Exit port, including upper transfer tray and lower "can-out" remote-transfer apparatus

3. External Equipment for Containment Box

- a. Manipulation -- Cell Interior
 - (1) Model 8 master-slave manipulators
 - (2) Extended-reach master-slave manipulators, used for transfers
 - (3) One-ton-capacity crane
 - (4) Through-wall transfer slide
- b. Transport
 - (1) Radio-controlled "mule" for transport of sample
 - (2) Robot manipulator for special transfers
- c. Utilities
 - Quick-connect bulkhead and regular fittings with double-end shut-off
 - (a) 1/4-in. ID for gas
 - (b) 3/8-in. ID for liquids
 - (2) Self-storing coil hose for some liquids and gases
 - (3) Halon-1301 fire-extinguisher system⁶
 - (4) AC-DC variable electricity
 - (5) Vacuum pump, light duty, for evaporation unit
 - (6) Neutron detector (235 U) mounted under containment box
 - (7) Remote one-gallon transfer system⁷

- Tellen 3-way stopcock valve nitrogen pressure line selector
 - F. Distilled water line containment box inlet
 - l. Plexiglas-shielded centrifuge
- rn. Exit port, including upper transfer tray and lower "can-out" remote-transfer apparalus

L. External Equipment for Containment Box

- Manipulation Cell Interior
- (1) Model 8 master-slave manipulator
- (2) Extended-reach master-slave manipulators, used for transfers
 - (3) One-ton-capacity crane
 - (4) Through-wall transfer slide

divogenarT .d

- (1) Radioscontrolled "mule" for transport of sample
 - (2) Robot manipulator for special transfers

c. Utilities

- (1) Outck-connect buildhead and regular littings with double-end shutt-off
 - (a) 1/4-in ID for gas
 - shippil tot (ll al-3) & (d)
 - 2) Self-storing coil hose for some liquids and gases
 - 3) Halon-1301 fire-extinguisher system
 - (4) AC-DC variable electricity
 - (5) Vacuum gump, light duty, for evaporation unit
 - (6) Neutron detector (220) mounted under containment box
 - (T) Remote one-gallon transfer system

ACKNOWLEDGMENT

The authors wish to thank Dr. S. Fried for his help in designing the evaporation system. The authors also wish to thank Mr. T. J. Meyer for help in construction of the containment box and Mr. Dale Henderson for performing the alpha pulse analyses.

THEORYSEN

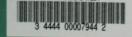
The authors wish to thank Dr. S. Fried for his help in designing the evaporation system. The authors also wish to thank Mr. T. J. Meyer for help in construction of the containment box and Mr. Dale Henderson for performing the alpha pulse analyses.

REFERENCES

- D. N. Metta, H. Diamond, and F. R. Kelley, J. Inorg. Nucl. Chem., in press.
- E. P. Horwitz, C. A. A. Bloomquist, and D. J. Henderson, J. Inorg. Nucl. Chem. 31, 1149 (1969).
- E. P. Horwitz, C. A. A. Bloomquist, D. J. Henderson, and D. E. Nelson, J. Inorg. Nucl. Chem., in press.
- D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Nucl. Chem. 4, 334 (1957).
- 5. H. F. Aly and R. M. Latimer, J. Inorg. Nucl. Chem. 29, 2041 (1967).
- T. E. Franck and C. H. Youngquist, "Fire Protection in Chemistry Hot Cells by Use of Halon-1301," Proceedings of the 15th Conference on Remote Systems Technology, p. 158 (1967).
- 7. H. W. Harvey and J. A. Buzzell, Containment Box Remote One-gallon Transfer System, to be published.

Shiri Barrista

- 1. D. N. Norra, H. Diamond, and V. F. Lulley, J. Inorg. Suci. Chem.
- E. P. Horwitz, C. A: A. Elocandist, and D. J. Senderson, J. Inorg. Nucl. Chem. 21, 1169 (1969).
- 3. E. P. Werelts, C. A. A. Bleonquist, D. J. Henderson, and D. E. Melson, J. Inorg. Augi. Chem., in press.
- A. D. E. Pepperd, G. M. Mason, J. L. Maier, and W. J. Driscoll, J. Inorg. Mucl. Cham. d, 338 (1987).
 - 5. B. E. Aly and R. M. barimer, J. Imorg. Sect. Chem. 59, 2041 (1967)
 - 6. T. E. Franck and C. H. Toungquist, "Fire Protection in Chesistiv Not Calls by Use of Halon-1301," Protections of the 15th Conformer on Secreta Systems Technology, p. 158 (1961).
 - H. W. Harrey and J. A. Buzzell, Containment, Bor Remota One-pailons Investigation Systems, to be published.



X

